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Si Atomic Layer Epitaxy Based on Si₂H₆ and Remote He Plasma Bombardment

by

A. Mahajan, J. Irby, D. Kinosky, R. Qian, S. Thomas, S. Banerjee, and A. Tasch

Department of Electrical and Computer Engineering

University of Texas at Austin

Austin, TX 78712

Tom Picraux

Sandia National Laboratories

Albuquerque, NM 87185

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Atomic layer Epitaxy(ALE) of Si has been demonstrated by using remote He plasma low energy ion bombardment to desorb H from a H-passivated Si(100) surface at low temperatures and subsequently chemisorbing Si ₂ H ₆ on the surface in a self-limiting fashion in a Remote Plasma Chemical Vapor Deposition(RPCVD) system in which the substrate is downstream from an r-f noble gas(He or Ar) glow discharge in order to minimize plasma damage. Remote He plasma bombardment for 1-3 min. was investigated over a range of temperatures (250°C-410°C), pressures (50-400 mTorr) and r-f powers (6-30 W) in order to desorb the H from the Si(100) surface and convert the (3x1) RHEED pattern to a (2x1) pattern which is characteristic of either a monohydride termination or a bare Si surface. Optimal He bombardment parameters were determined to be 30 W at 100 mTorr process pressure at 400°C for 1-3 min. The He bombardment cycles were followed by Si ₂ H ₆ dosing over a range of partial pressures (10 ⁻⁷ Torr to 1.67 mTorr), temperatures (250°C-400°C) and times (20 s to 3 min.) without plasma excitation, because it is believed that Si ₂ H ₆ can chemisorb in a self-limiting fashion on a bare Si surface as 2 silyl (SiH ₃) species, presumably leading to a H-terminated surface once again. Alternate Si ₂ H ₆ dosing and He low energy ion bombardment cycles (-100-200) were performed to confirm the ALE-mode of growth. It was found that the growth per cycle saturates with long Si ₂ H ₆ dosing at a level which increases slightly with He bombardment time. At 400°C, for 2 min. He bombardment at 100 mTorr and 30 W, the growth per cycle saturates at ~0.1 monolayers/cycle, while for 3 min. He bombardment, the Si growth saturates at ~0.15 monolayers/cycle.					
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Bombardment**

**A.Mahajan, J.Irby, D.Kinosky, R.Qian, S.Thomas, S.Banerjee, A.Tasch and
T.Picraux*.**

Department of Electrical and Computer Engineering, ENS415, University of Texas,

Austin TX 78712

***Sandia National Laboratories, Albuquerque NM 87185**

Phone: (512)-471-4514

FAX: (512)-471-8575.

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ABSTRACT

Atomic layer Epitaxy(ALE) of Si has been demonstrated by using remote He plasma low energy ion bombardment to desorb H from a H-passivated Si(100) surface at low temperatures and subsequently chemisorbing Si₂H₆ on the surface in a self-limiting fashion. Si substrates were prepared using an RCA clean followed by a dilute HF dip to provide a clean, dihydride-terminated (1x1) surface, and were loaded into a Remote Plasma Chemical Vapor Deposition(RPCVD) system in which the substrate is downstream from an r-f noble gas(He or Ar) glow discharge in order to minimize plasma damage. An *in situ* remote H plasma clean at 250°C for 45 min. was used to remove surface O and C and provide an alternating monohydride and dihydride termination, as evidenced by a (3x1) RHEED pattern. It was found necessary to desorb the H from the Si surface to create adsorption sites for Si-bearing species such as Si₂H₆. Remote He plasma bombardment for 1-3 min. was investigated over a range of temperatures (250°C-410°C), pressures (50-400 mTorr) and r-f powers (6-30 W) in order to desorb the H and convert the (3x1) RHEED

pattern to a (2x1) pattern which is characteristic of either a monohydride termination or a bare Si surface. It was found that as He pressures and r-f powers are raised the plasma potential and mean free paths are reduced, leading to lower He bombardment energies but higher fluxes. Optimal He bombardment parameters were determined to be 30 W at 100 mTorr process pressure at 400°C for 1-3 min. He was found to be more effective than Ar bombardment because of the closer match of the He and H masses compared to that between Ar and H. Monte Carlo TRIM simulations of He and Ar bombardment of H-terminated Si surfaces were performed to validate this hypothesis and to predict that approximately 3 surface H atoms were displaced by the incident He atoms, with no bulk Si atom displacement for He energies in the range of 15-60 eV. The He bombardment cycles were followed by Si₂H₆ dosing over a range of partial pressures (10⁻⁷ Torr to 1.67 mTorr), temperatures (250°C-400°C) and times (20 s to 3 min.) without plasma excitation, because it is believed that Si₂H₆ can chemisorb in a self-limiting fashion on a bare Si surface as 2 silyl (SiH₃) species, presumably leading to a H-terminated surface once again. The Si₂H₆ dosing pressures and times corresponded to saturation dosing (~10⁶ Langmuirs). Alternate Si₂H₆ dosing and He low energy ion bombardment cycles (~100-200) were performed to confirm the ALE-mode of growth. It was found that the growth per cycle saturates with long Si₂H₆ dosing at a level which increases slightly with He bombardment time. At 400°C, for 2 min. He bombardment at 100 mTorr and 30 W, the growth per cycle saturates at ~0.1 monolayers/cycle, while for 3 min. He bombardment, the Si growth saturates at ~0.15 monolayers/cycle. It was also confirmed that the growth is achieved only by using alternate He bombardment and Si₂H₆ dosing. Helium bombardment alone for a comparable time (3 min. x100 cycles) causes a negligible change of the Si film thickness (<5Å). Similarly, thermal growth using Si₂H₆ under these conditions for (3 min. x100 cycles) causes negligible deposition (<5Å).

INTRODUCTION

Precise control of doping and hetero-structures is extremely important for next-generation Si Ultra Large Scale Integrated(ULSI) devices. Such a capacity can maintain compact doping profiles and fabricate the abrupt hetero-interfaces required for "ordered" Si_mGe_n superlattices which will require "digital" control over layer thicknesses. Delta doped structures will require atomic plane doping which is possible only by Atomic Layer Epitaxy (ALE) techniques. The basic technique consists of use of surface chemical reactions for getting layer-by-layer growth. ALE of III-V compounds has been widely demonstrated by alternately introducing gaseous reactants into the reaction chamber [1]. ALE of Column IV materials poses certain unique difficulties. Passivation of the surface to inhibit adsorption of the species in between depositions is required. Hydrogen coverage is an attractive passivation technique as it is relatively easy to attain and sometimes the only passivation technique obtainable. The H needs to be removed from the surface to open up surface adsorption sites for the next cycle of deposition. Thermal means have been effectively used for H removal either by heating the whole substrate, as in Rapid Thermal Processing (RTP), or in a localized fashion as in Laser Induced Thermal Desorption(LITD). In the current approach we have used low energy noble gas ion bombardment from a r-f plasma for H removal from the Si surface.

Germanium ALE has been reported by using $\text{Ge}(\text{C}_2\text{H}_5)_2\text{H}_2$ with the ethyl group as the surface passivating species [2]. Extension of this method to Si is known to create C contamination problems. Si Molecular Layer Epitaxy using RTP with SiH_2Cl_2 and H_2 gases has been reported [3]. This is a high temperature process with transient temperatures rising to as high as 1100K. In addition, a halogenic approach is incompatible with Ultra High Vacuum (UHV). Si_2H_6 has been successfully used as a precursor for ALE, using LITD of H [4]. But large area growth is difficult with an excimer laser.

In our approach, a remote H plasma clean was used to initially get a stable H-terminated Si surface. This H was then removed to create adsorption sites by He ion bombardment from a remote r-f He plasma. The surface was then dosed with the Si bearing precursor, Si_2H_6 , which chemisorbs in a self-limiting manner and restores the H-passivated surface. The H is removed again by He ion bombardment in the next cycle to create adsorption sites.

EXPERIMENTAL PROCEDURE

The schematic of the RPCVD system used for the *in situ* remote H plasma clean and ALE growth is shown in Fig.1. The system consists of three interconnected Ultra High Vacuum (UHV) chambers: a load lock chamber for sample loading with a base pressure of 3×10^{-9} Torr, a surface analysis chamber with a base pressure of 2×10^{-10} Torr equipped with an Auger Electron Spectroscopy (AES) system for *in situ* monitoring of surface contamination, and a process chamber with a base pressure of 5×10^{-9} Torr equipped with a r-f plasma source in which the remote H plasma clean and epitaxial growth are performed. The deposition chamber is equipped with a Residual Gas Analyzer (RGA) to allow monitoring of the background levels of oxygen and water in the ambient, as well as to monitor the various species during processing using a differential pumping scheme. A Reflection High Energy Electron Diffraction (RHEED) system in the process chamber allows *in situ* diagnostics of surface reconstruction and crystallinity. Ultra-high purity gases are used in the process, in which the partial pressures of water and oxygen were 1×10^{-9} Torr and 5×10^{-11} Torr, respectively. To further reduce the oxygen and water vapor in the process gases, all gas lines are equipped with Nanochem gas purifiers which reduce the oxygen and water vapor to the parts-per-billion level [5]. The wafers used are 75 mm diameter lightly doped p-type Si(100) substrates. Before wafers were loaded into the system, they were

cleaned using a wet chemical treatment consisting of an ultrasonic degrease in TCA, acetone, and methanol. A subsequent ultra-high purity water rinse was followed by a modified RCA clean for removal of organic and metallic contamination. A 60s 40:1 H₂O:HF dip was used to remove the oxide grown during the RCA clean. After a final 20:1 H₂O:HF dip for 30s. the wafers were spun dry, and immediately placed in a nitrogen-purged glove box and loaded into the load lock chamber. Prior to the process, the wafers were cleaned *in situ* using a remote H plasma clean to remove carbon and oxygen contamination [6]. For a typical clean, 200 sccm of H is introduced at the base of the plasma column at a pressure of 50 mTorr and inductively excited with 9 W of r-f power (13.56 MHz). During the clean, which lasts 45 minutes, the substrate is heated to 250 C from the back using a boron nitride heater. RHEED analysis of wafers cleaned by the above technique show 1/3-order streaks (Fig. 2a) indicative of a (3x1) reconstruction pattern. The (3x1) reconstruction pattern has been found to be due to alternating monohydride and dihydride termination [7]. This surface was then bombarded with He or Ar ions from the plasma over a range of temperatures (250°C-410°C), pressures (50-400 mTorr) and r-f powers (6-30 W) in order to desorb the H and convert the (3x1) RHEED pattern to a (2x1) pattern which is characteristic of either a monohydride termination or a bare Si surface.

The ALE growth was started on this H-passivated surface which consisted of 100-200 repetitions of the deposition cycle. Each cycle consisted of He plasma bombardment to desorb H after which the r-f power was switched off and Si₂H₆ was introduced into the chamber through a gas feed ring at a flow rate and for a time required to produce the required dose. This was followed by a pumpdown time of 30 s during which the Si₂H₆ flow was shut off and was flushed out of the system before starting the next He bombardment cycle.

RESULTS AND DISCUSSION

Fig.3. shows the parameter space in which H desorption was obtained by the above method as was evidenced by the change of the (3x1) RHEED pattern to a (2x1) pattern. It was seen that there is a certain optimum range of plasma powers for an effective H removal from the Si surface. This range gets narrower at higher pressures. It was determined from Langmuir probe measurements that as r-f power is increased the ion flux increases but the plasma potential and hence the bombardment energy decreases. Also, as the pressure is increased, the ion free path decreases and the bombardment energy decreases although the ion density goes up. The inability of He bombardment to desorb H from the surface at low powers was presumed to be due to low ion fluxes at low powers. On the other hand as the plasma potential decreases with increasing r-f power, the bombarding ions lack the energy for effective removal of the H from the surface at high r-f powers. The energy of the bombarding ions also decreases with increasing pressure due to decreasing mean free path. Thus it was more difficult to remove H from the surface at higher pressures. The optimal plasma power for H desorption at a given process pressure was chosen to be in the middle of the r-f power range.

For the ALE cycles, the process pressure during the bombardment was chosen to be 100 mTorr, where the optimum range of r-f plasma powers is rather wide. The temperature was kept constant at 400°C during the process. This places the temperature below the β_2 peak of the Temperature Programmed Desorption (TPD) curve of H, Fig.4. [8], thus ensuring that there was no significant H desorption from the surface during the process by thermal means. 30W of r-f power was used to excite the He plasma. The bombardment time was varied from 1 to 3 minutes with different amounts of dosing for each bombardment duration. The results are shown in Fig.5. As the Si_2H_6 dosing is increased for the same amount of He bombardment, the amount of growth increases initially. In this regime it is

believed that the growth is limited by the availability of Si₂H₆. As the Si₂H₆ dosing increased the growth is limited by the extent of H desorption from the Si surface by the He ion bombardment, as evidenced by an increase in the growth rate from 0.06 ML/cycle for a dosing of 9x10⁴ Langmuirs to a saturation growth rate of ~0.11 ML/cycle at higher doses (for a He bombardment time of 2 min.). Thus, the growth rate follows the general trend of saturation at higher doses for a given He bombardment time. Also the amount of growth in the saturation region increases with the He bombardment time. A plot of the Si growth rate versus the He bombardment time for a given amount of dosing shows an increase in the growth rate with the time of He bombardment (Fig.6.). It can be seen that the saturation growth rate increases from ~0.1 ML/cycle for 2 min. He bombardment to ~0.15 ML/cycle for 3 min. He bombardment, thus leading to the inference that the amount of H desorption is increased by increasing the He bombardment time. This can be used to control the extent of H desorption and hence the growth rate.

The films grown by ALE are smooth and single crystal. This is indicated by RHEED analysis which shows a streaky (2x1) reconstruction pattern after growth (Fig.7.).

It might also be mentioned that it was confirmed that the growth observed in these experiments was not due to purely thermal growth of Si from Si₂H₆ or due to sputtering of Si from the chamber wall deposits during He plasma bombardment both of which resulted in negligible growth (<5Å) for a comparable duration.

Monte Carlo TRIM simulations were performed to estimate the number of H and Si atoms displaced by the incident He and Ar ions [9]. An amorphous Si substrate with a monolayer coverage of H is assumed as the starting material and is bombarded with normal incidence He or Ar ions. No crystallographic information is included in the model. Sharp displacement thresholds for bulk and surface atoms are assumed. The displacement energy is 3 eV for the surface H atoms and 22 eV

for the bulk Si atoms. A target atom which receives a recoil energy greater than the displacement energy is assumed to be displaced. Helium ions are found to be more effective for removal of H atoms from the substrate than Ar ions. The number of H atoms from the surface displaced by ion bombardment increases to about 3 displacements per incident He ion with increasing ion energy in the 10-70 eV range, which corresponds to typical values of the plasma potential in RPCVD. The number is lower for Ar ion bombardment (Fig.8.). There is more Si atom displacement in the underlying Si substrate by Ar ions (~0.11 Si displacements per Ar ion at 45 eV) compared to negligible displacement by He ions (0.003 Si displacements per He ion at 70 eV). This indicates that there is a wider process window for He than for Ar in which H can be desorbed from the Si surface without creating subsurface damage. This is believed to be due to the fact that the He mass is more closely matched to the H mass than Ar, while the mismatch with the Si mass is greater for He.

CONCLUSIONS

We have demonstrated removal of H from a H-passivated Si(100) surface by low energy (~50eV) He ion bombardment. The extent of the removal of H from the surface can be controlled by varying the duration of He bombardment and plasma parameters. This, in turn, means that the growth rate by this method can also be controlled. Si_2H_6 was shown to adsorb in a self-limiting manner on the Si(100) surface.

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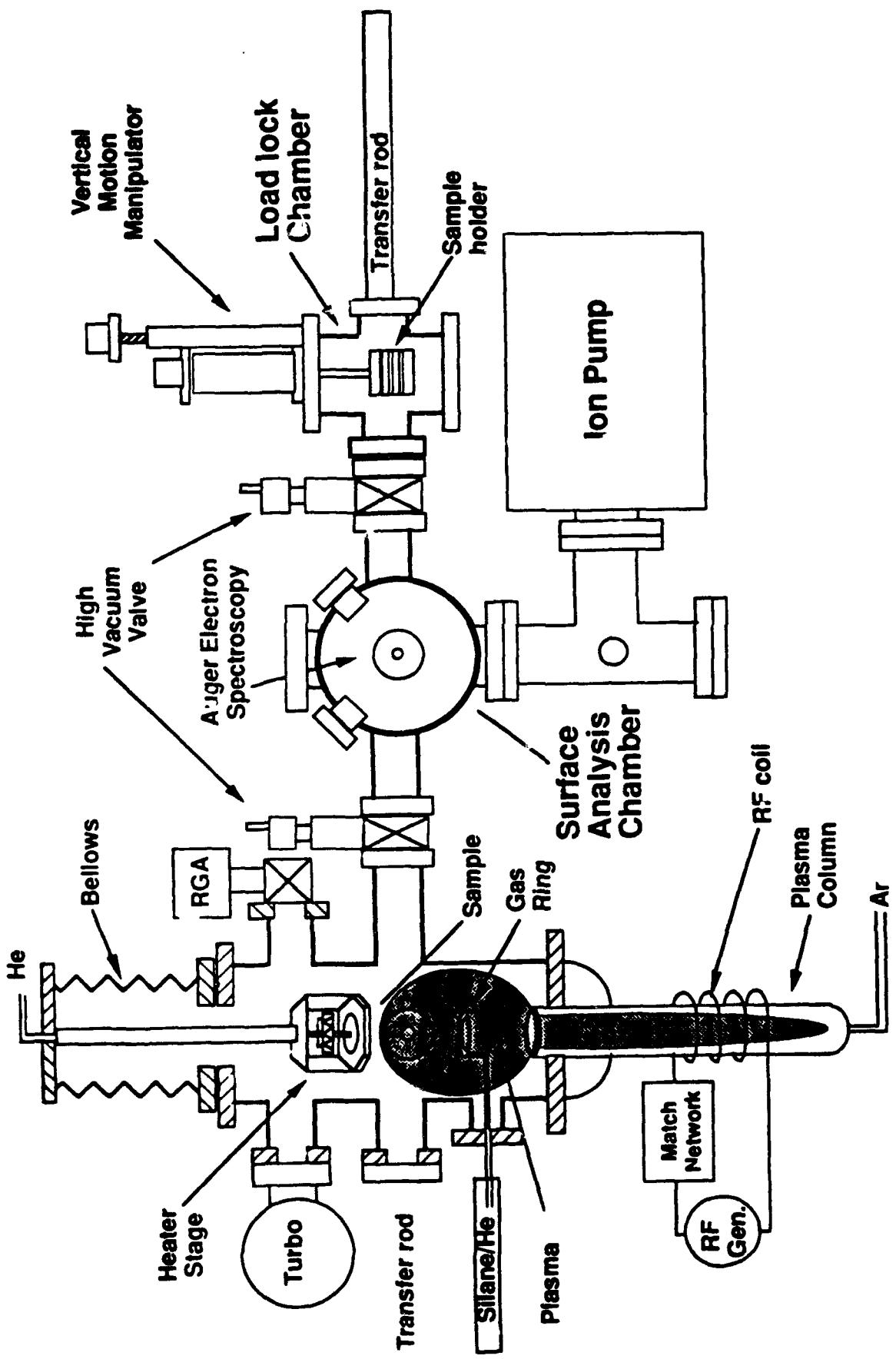
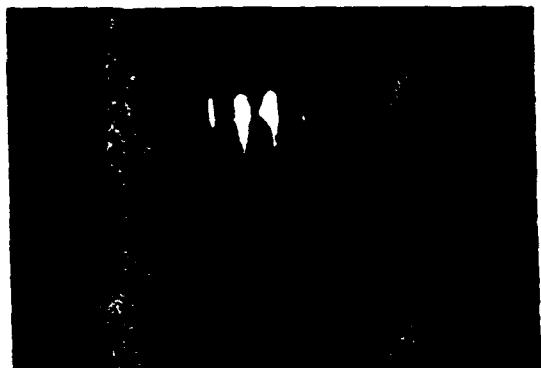


Fig.1. RPCVD System Schematic



(a)



(b)

Fig. 2 RHEED analysis showing removal of hydrogen by He ion bombardment. Fig. (a) shows the (3x1) reconstruction after remote H plasma clean, while Fig. (b) shows that the surface reconstruction has converted to (2x1) after 1 min. of He ion bombardment.

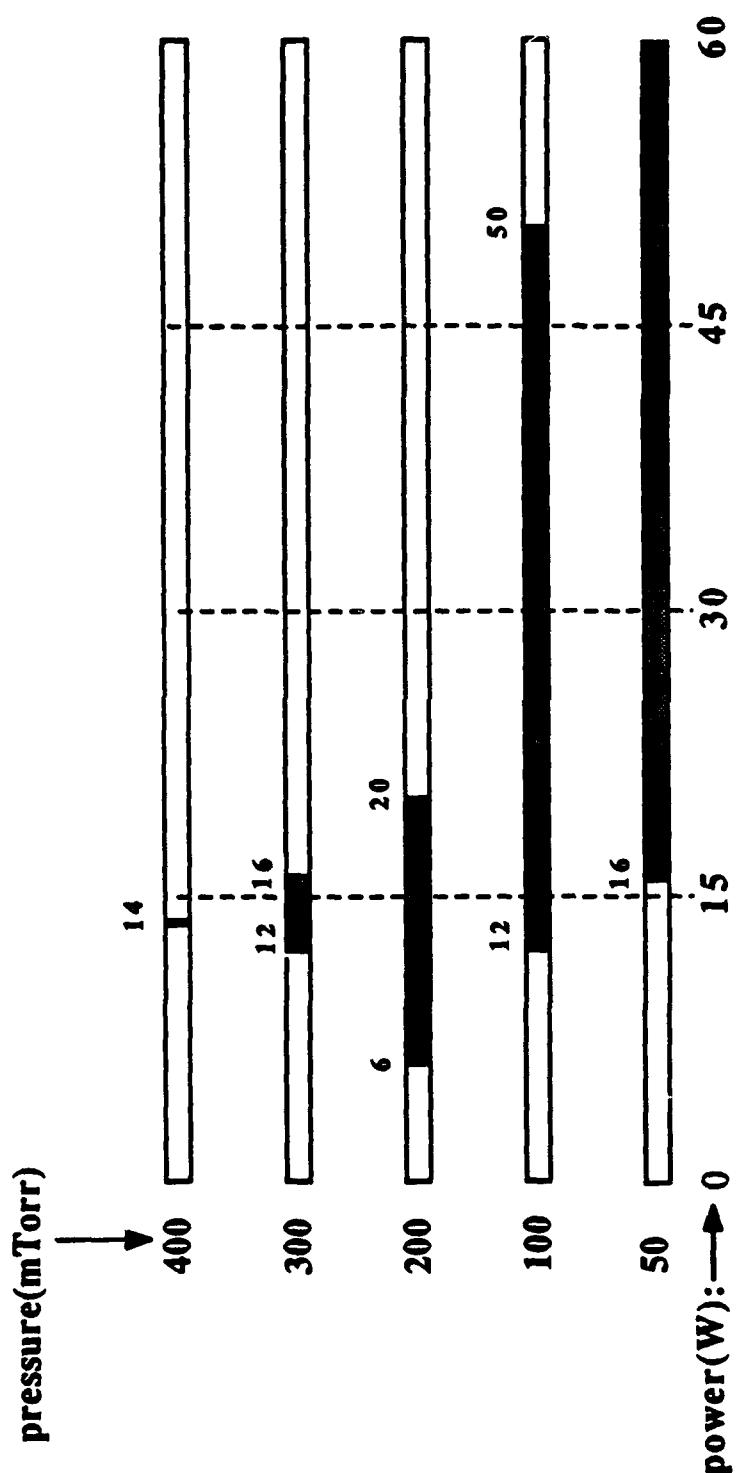


Fig.3. Darkened areas show range of plasma powers at various pressures for effective removal of H from Si(100) surface at 250°C for bombardment times of 1-2 min. as evidenced by RHEED.

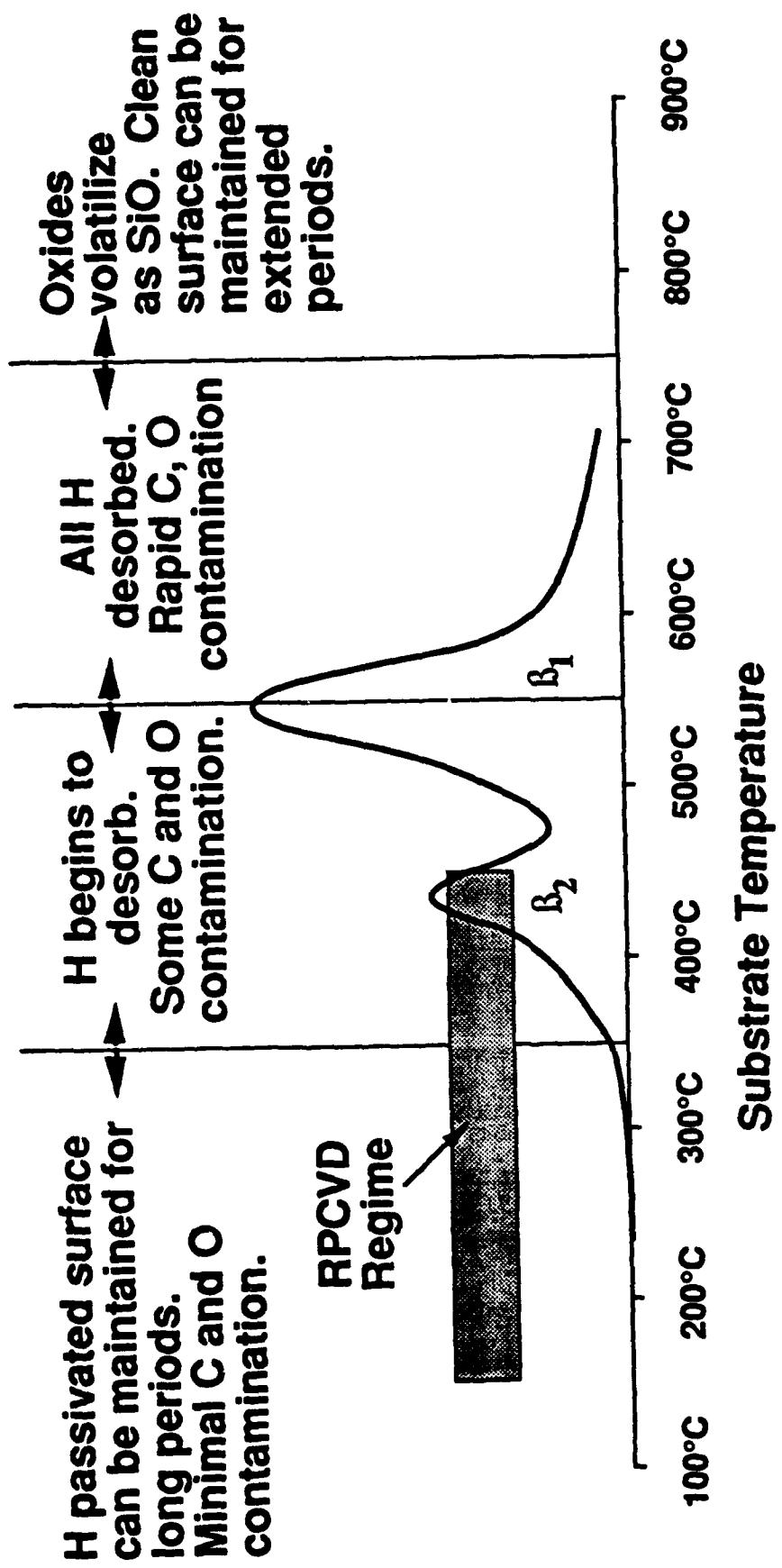


Fig.4. H passivation as a function of temperature. TPD data from Ref.8.

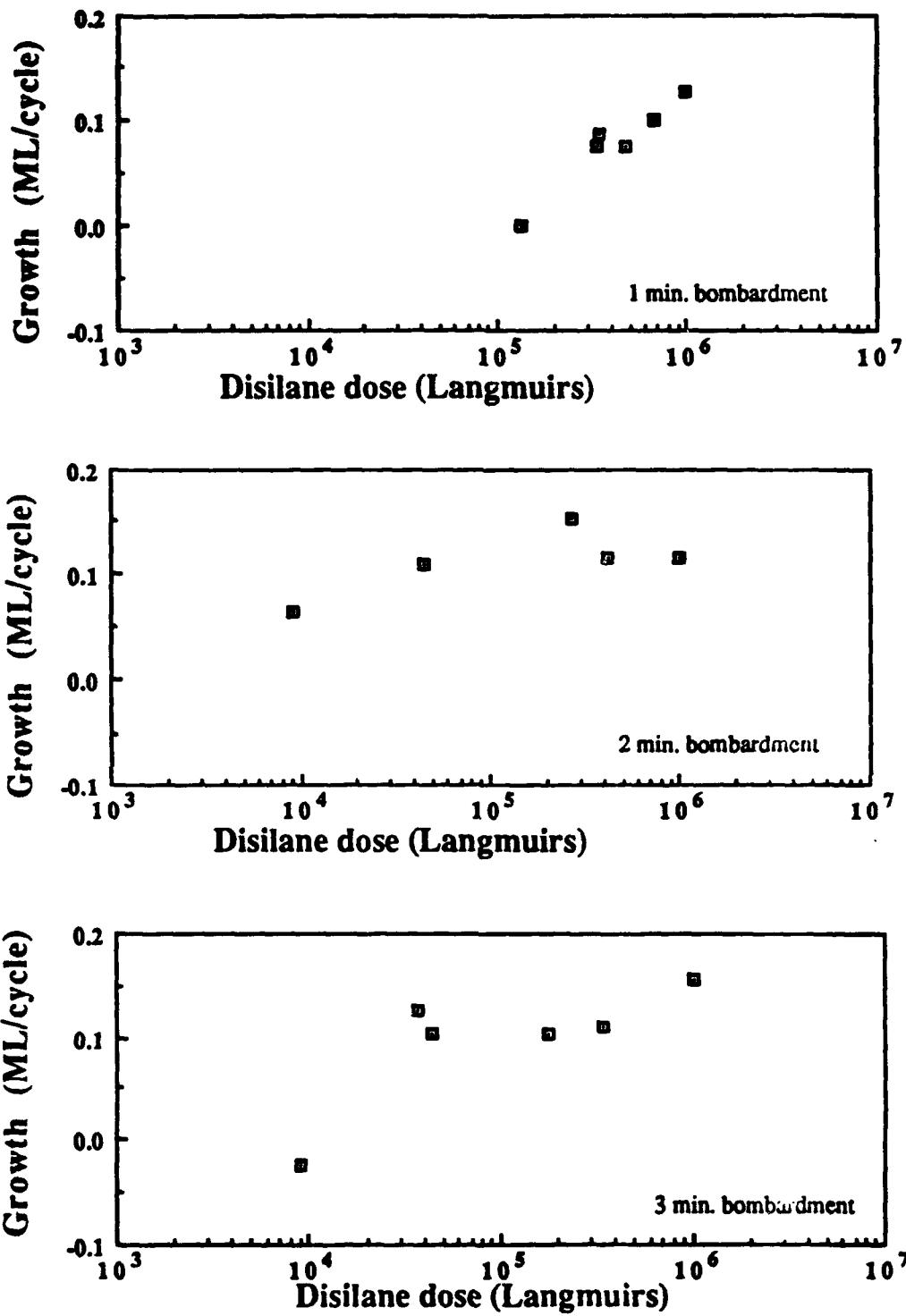


Fig.5. Plot of growth versus disilane dose for bombardment times of 1,2 and 3 minutes.

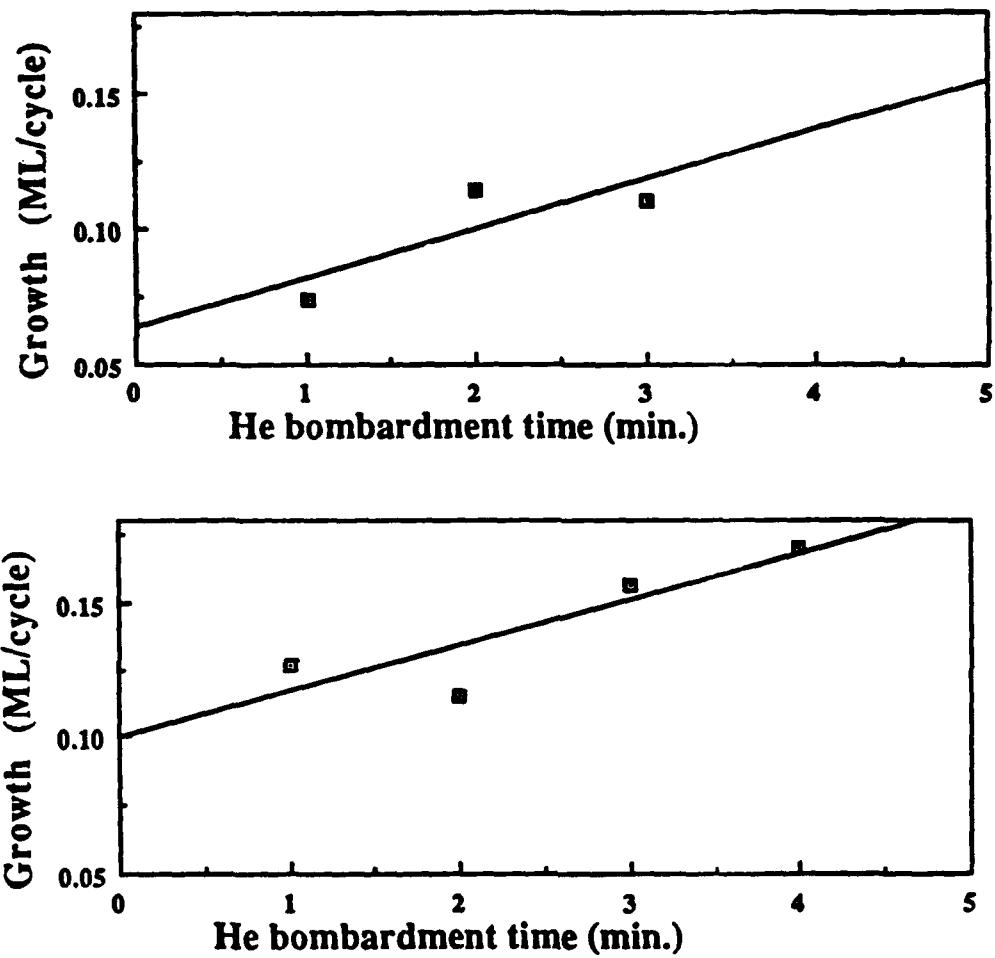


Fig.6. Plot of growth versus He bombardment time for disilane dose of (a) 4×10^5 Langmuirs (b) 1×10^6 Langmuirs.

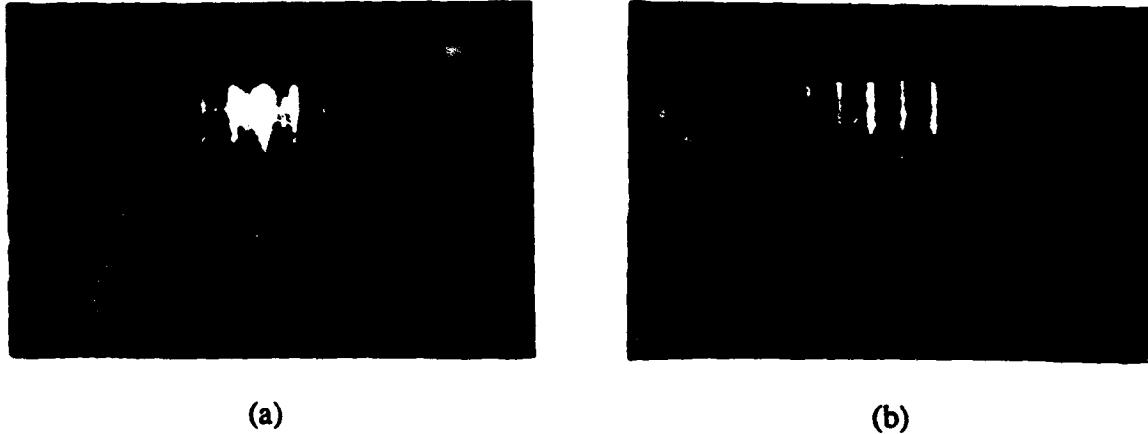


Fig. 7 RHEED analysis of films grown by ALE showing that the films are high quality single crystal. Fig. (a) shows the pattern before deposition and Fig. (b) is after 100 cycles of ALE growth at 400°C, 100 mTorr pressure, 2min. He bombardment at 30W plasma power. Disilane dosing was 1.0×10^6 Langmuirs per cycle.

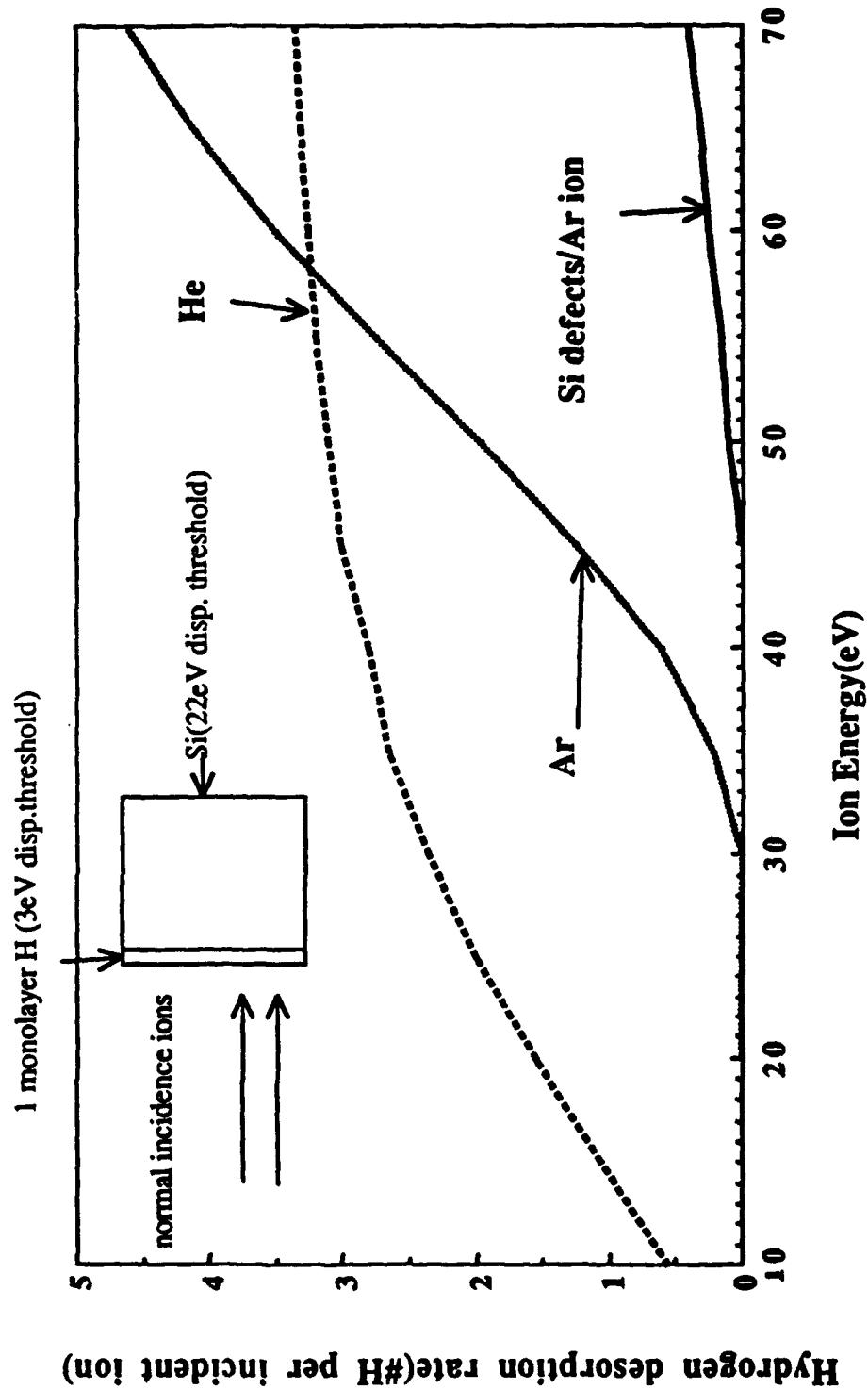


Fig.8. Monte Carlo TRIM simulations of H displacement rate versus energy of incident ions(He and Ar)